

d & f-BLOCK ELEMENTS

2.0 INTRODUCTION :

- (i) d-block elements are often called as 'transition elements' because their position in periodic table is between the s-block and p-block elements.
- (ii) Their properties are transitional between the highly reactive metallic elements of s-block (which form ionic compounds) and the elements of p-block (which are largely covalent).
- (iii) Typically the transition elements have an incompletely filled d-orbital. A transition element may be defined as the element whose atom in ground state or ion in one of common oxidation states, has partly filled d-sub shell i.e. having electrons between 1 to 9.
- (iv) Group 12 (the zinc group) elements have completely filled d-orbitals in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.
- (v) The general electronic configuration of d-block elements is $(n-1) d^{1-10} ns^{1-2}$, where n is the outer most shell. However, palladium does not follow this general electronic configuration. It has electron configuration $[Kr]^{36} 4d^{10} 5s^0$ in order to have stability.
- (vi) Zn, Cd and Hg are involved in transition series but they are called non transition elements due to completely filled d-orbitals.

| 1st Series | | | | | | | | | | |
|------------|----|----|----|----|----|----|----|----|----|----|
| Z | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| 4s | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 2 | 1 | 2 |
| 3d | 1 | 2 | 3 | 5 | 5 | 6 | 7 | 8 | 10 | 10 |

| 2nd Series | | | | | | | | | | |
|------------|----|----|----|----|----|----|----|----|----|----|
| Z | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| 5s | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 2 |
| 4d | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 10 | 10 |

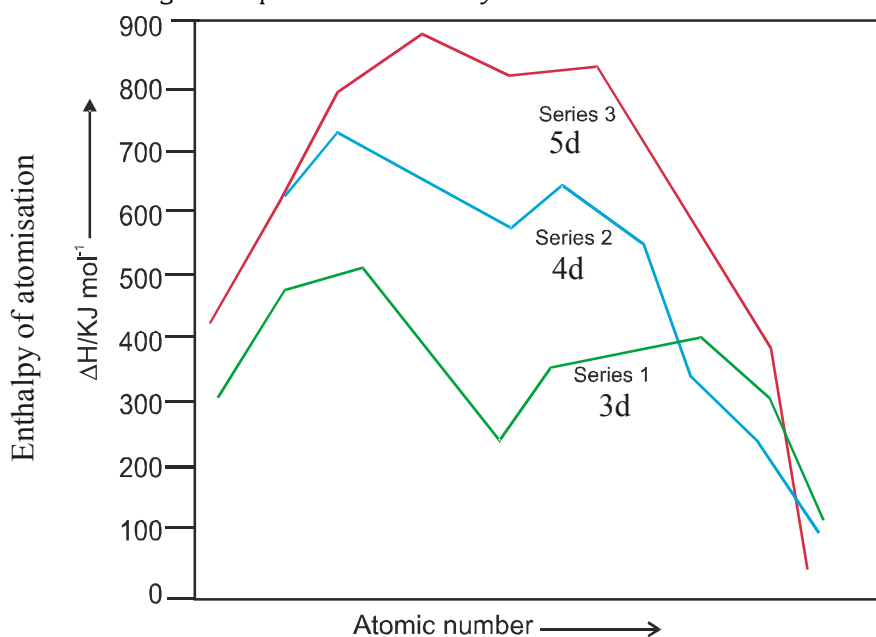
| 3rd Series | | | | | | | | | | |
|------------|----|----|----|----|----|----|----|----|----|----|
| Z | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
| | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| 6s | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 1 | 2 |
| 5d | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 9 | 10 | 10 |



2.1 GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

(A) Metallic character :

- (i) In d-block elements the last but one (i.e. the penultimate) shell of electrons is expanding. Thus they have many physical and chemical properties in common.
- (ii) Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
- (iii) Most transition elements have ccp/hcp type structures.
- (iv) The transition elements are very much hard and have low volatility, they have high enthalpy of atomisation.
- (v) Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomisation in their respective period.
- (vi) The metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions.
- (vii) The metals of the 4d and 5d series have greater enthalpies of atomisation than the corresponding elements of the 3d and this is an important factor indicating for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.



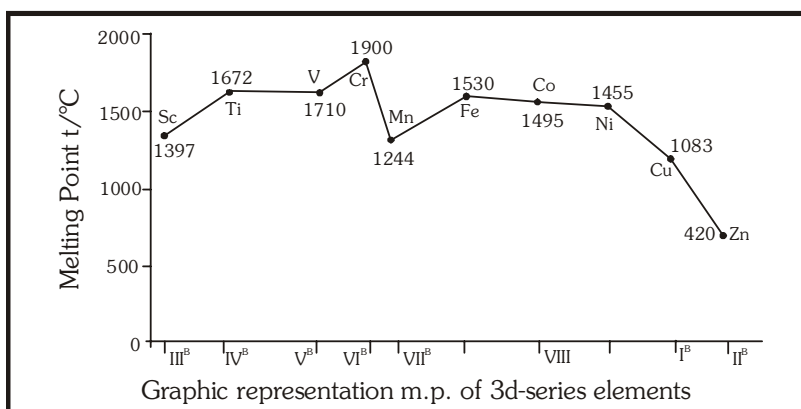
Graph showing Trends in enthalpies of atomisation of transition elements

(B) MELTING AND BOILING POINTS

- (i) Melting and boiling point of d-block > s-block
Reason : Stronger metallic bond formed present by unpaired d-electrons.
- (ii) In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond melting and boiling point are very low in series. (Volatile metals Zn, Cd, Hg)
- (iii) In 3d series Sc to Cr melting and boiling point increases then Mn to Zn melting and boiling point decreases
- (iv) As the number of unpaired d-electron increases, the number of covalent bond and bond energy between the atoms is expected to increase up to Cr-Mo-W family where each of the d-orbital has only unpaired electron and the opportunity for covalent sharing is greatest.



- (v) Mn and Tc have comparatively low melting point, due to weak metallic bond because of stable Half filled (d5) configuration and high IP.
- (vi) Lowest melting point Hg (-38°C) ; Highest melting point W ($\approx 3400^{\circ}\text{C}$)



Illustrations

Illustration 1 : Why do the transition elements have higher boiling & melting points ?

Solution Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

(C) DENSITY :

- The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased effective nuclear charge. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high.
- Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities also increase across a period.

$$\text{Sc} \leq \text{Ti} \leq \text{V} \leq \text{Cr} \leq \text{Mn} \leq \text{Fe} \leq \text{Co} \leq \text{Ni} \approx \text{Cu} > \text{Zn}$$

(zinc is an exception, having large atomic volume and hence has lower density)

- $3d < 4d < 5d$ Series

- Maximum density : $\text{Ir} \geq \text{Os}$

(D) Ionisation energies or Ionisation enthalpies :

- The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled $(n-1) d^{10} ns^2$ configuration.
- Order of second ionisation energy : $\text{Sc} < \text{Ti} < \text{V} < \text{Mn} < \text{Cr}$

(E) Oxidation states :

- The transition metals exhibit a large number of oxidation states. With the exception of a few elements, most of these show variable oxidation states. These different oxidation states are related to the electronic configuration of their atoms.
- The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner $(n-1)$ d-electrons in addition to outer ns-electrons because, the energies of the ns and $(n-1)$ d-sub-shells are nearly same.
- In general oxidation state of d-block element is given as
 minimum oxidation state = number of 's' electrons
 maximum oxidation state = number of 's' electrons + unpaired 'd' electron



Different oxidation states of first transition series.

| Element | Outer electronic configuration | Oxidation states |
|---------|--------------------------------|--------------------------|
| Sc | $3d^1 4s^2$ | +3 |
| Ti | $3d^2 4s^2$ | +2, +3, +4 |
| V | $3d^3 4s^2$ | +2, +3, +4, +5 |
| Cr | $3d^5 4s^1$ | +2, +3, (+4), (+5), +6 |
| Mn | $3d^5 4s^2$ | +2, +3, +4, (+5), +6, +7 |
| Fe | $3d^6 4s^2$ | +2, +3, (+4), (+5), (+6) |
| Co | $3d^7 4s^2$ | +2, +3, (+4) |
| Ni | $3d^8 4s^2$ | +2, +3, +4 |
| Cu | $3d^{10} 4s^1$ | +1, +2 |
| Zn | $3d^{10} 4s^2$ | +2 |

• Oxidation states given in parenthesis are unstable.

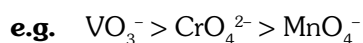
Higher oxidation state in d-block = +8 (Os, Ru)

Zero oxidation state for e.g. $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$

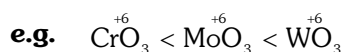
(iv) Relative stability of oxidation state :

| | |
|-----------------------------------|---|
| $\text{Sc}^{+2} < \text{Sc}^{+3}$ | inert gas stable configuration |
| $\text{Ti}^{+3} < \text{Ti}^{+4}$ | |
| $\text{Mn}^{+6} < \text{Mn}^{+7}$ | |
| $\text{V}^{+4} < \text{V}^{+5}$ | |
| $\text{Mn}^{+3} < \text{Mn}^{+2}$ | d^5 stable configuration |
| $\text{Cr}^{+2} < \text{Cr}^{+3}$ | d^3 is more stable than d^4 in aq. solution |
| $\text{Ni}^{+2} > \text{Ni}^{+4}$ | On the basis of sum of first four I.P's. |
| $\text{Pt}^{+2} < \text{Pt}^{+4}$ | |

(v) On moving in a period stability of higher oxidation state decreases

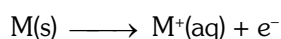


(vi) On moving down the group stability of higher oxidation state increases

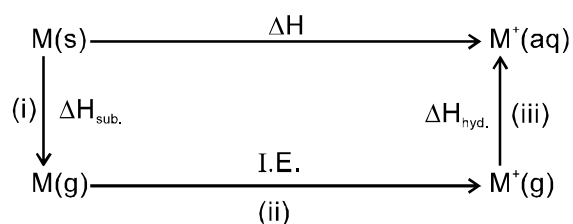


(F) ELECTRODE POTENTIALS :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:



This process actually takes place in the following three steps as given in following flowchart :



The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is $\Delta H = \Delta_{\text{sub}} H^\ominus + \Delta H + \Delta_{\text{hyd}} H$

If SOP is +ve \rightarrow Means Oxidation easy

If SRP is +ve \rightarrow Means reduction easy

Some important examples :

1. $E_{\text{M}^{2+}/\text{M}}^0 \Rightarrow$ +ve only for Cu among 3d elements because HE of Cu^{+2} is not enough to compensate for sublimation energy, IP_1 and IP_2 for Cu.

2. $E_{\text{M}^{3+}/\text{M}^{2+}}^0 \Rightarrow$

(a) $E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^0 = -ve$

Reason : $t_2g^3 eg^0 \leftarrow d^3 > d^4$

(b) $E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^0 = +ve \text{ (high)}$

Reason : $d^4 < d^5$

(c) $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = \text{less +ve (learn)}$

Reason : $d^5 > d^6$

Note : The SRP of $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0$ is less than expected because of extra stability of d^5 configuration of Fe^{+3} ion.

(G) TRENDS IN STABILITY OF HIGHER OXIDATION STATES

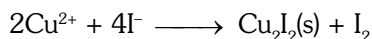
Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element. The highest oxidation states are shown generally among halides and oxides.

Halides of first transition series

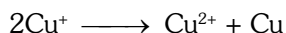
- In metal halides.** The transition elements react with halogens at high temperatures to form transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ; $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.
- Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX_4 (tetrahalides, $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I), VF_5 and CrF_6 .



- (iv) The +7 oxidation state for Mn is not shown by simple halides. However, MnO_3F is known in which the oxidation state of Mn is +7.
- (v) The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy due to higher covalent bonds e.g., VF_5 and CrF_6 .
- (vi) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only VX_2 (X = Cl, Br or I) and copper can form CuX (X = Cl, I). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I⁻ to I_2 .



It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :



Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ($\Delta_{\text{hyd}}H^\ominus$) of Cu^{2+} (aq) than Cu^+ , which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

(H) IN METAL OXIDES AND OXOCATIONS.

- (i) The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides coincides with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides, Sc_2O_3 whereas the highest oxidation state of manganese of group 7 is +7, in Mn_2O_7 .
- (ii) Besides the oxides, oxocation of the metals also stabilise higher oxidation states. For example, V^V as VO_2^+ , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} .
- (iii) It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as MnF_4 whereas the highest oxide is Mn_2O_7 . This is due to the fact that oxygen has great ability to form multiple bonds to metals.
- (iv) The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g., in MnO_4^- all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn, Mn_2O_7 is a covalent. In these higher oxides the acidic character is predominant. Thus CrO_3 gives H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$ and Mn_2O_7 gives HMnO_4 . **V_2O_5 is, however amphoteric though mainly acidic and with alkalis as well as acids gives VO_4^{3-} and VO_2^+ respectively.**

In general

| Oxidation state | Nature of oxide/Hydroxide (d-block) |
|-----------------|-------------------------------------|
| +1, +2, +3 | Basic |
| +4 | Amphoteric |
| +5, +6, +7, +8 | Acidic |

Except Cr_2O_3 = Amphoteric

(I) **FORMATION OF COLOURED IONS** : See coordination compound

(J) **MAGNETIC PROPERTIES**

It is interesting to note that when the various substances are placed in a magnetic field, they do not behave in a similar way i.e., they show different behaviour which are known as magnetic behaviour.

These are classified as :



- (i) **Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.
- (ii) **Diamagnetic substances.** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals. Most of the compounds of transition elements are paramagnetic in nature and are attracted by the magnetic field.
- The transition elements involve the partial filling of d-sub-shells. Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration d^1 to d^9) and therefore, they give rise to paramagnetic character.
- (iii) The magnetic moment arise only from the spin of the electrons. This can be calculated from the relation $\mu = \sqrt{n(n+2)}$ B.M. n = Number of unpaired electrons

Table : Calculated and Observed Magnetic Moments (BM)

| Ion | Configuration | Unpaired electron(s) | Magnetic moment | |
|------------------|------------------|----------------------|-----------------|-----------|
| | | | Calculated | Observed |
| Sc ³⁺ | 3d ⁰ | 0 | 0 | 0 |
| Ti ³⁺ | 3d ¹ | 1 | 1.73 | 1.75 |
| Ti ²⁺ | 3d ² | 2 | 2.84 | 2.76 |
| V ²⁺ | 3d ³ | 3 | 3.87 | 3.86 |
| Cr ²⁺ | 3d ⁴ | 4 | 4.90 | 4.80 |
| Mn ²⁺ | 3d ⁵ | 5 | 5.92 | 5.96 |
| Fe ²⁺ | 3d ⁶ | 4 | 4.90 | 5.3 – 5.5 |
| Co ²⁺ | 3d ⁷ | 3 | 3.87 | 4.4 – 5.2 |
| Ni ²⁺ | 3d ⁸ | 2 | 2.84 | 2.9 – 3.4 |
| Cu ²⁺ | 3d ⁹ | 1 | 1.73 | 1.8 – 2.2 |
| Zn ²⁺ | 3d ¹⁰ | 0 | 0 | |

(K) **FORMATION OF COMPLEXES :** See coordination compound

(L) **FORMATION OF INTERSTITIAL COMPOUNDS**

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms as shown below.

e.g. WC, Fe₃C, TiH_{1.30 – 1.80}

Properties :

- (1) They are generally non-stoichiometric compound.
- (2) Neither typical ionic nor covalent
- (3) Harder than pure metal
- (4) High melting point than pure metal
- (5) Malleability and ductility less than pure metal
- (6) Chemically inert

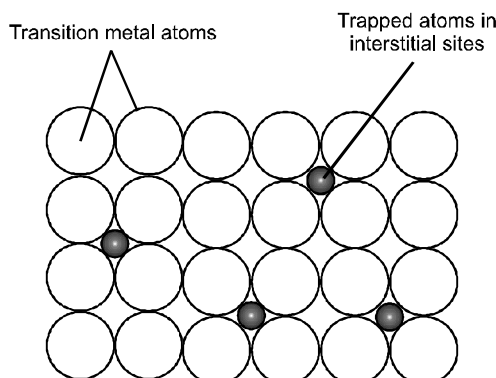


Figure showing formation of interstitial compounds

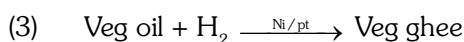
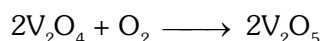
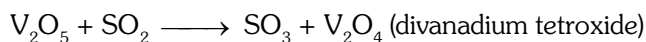
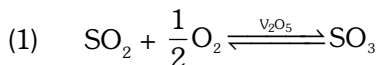


(M) CATALYTIC PROPERTIES

d-block metals or their compound act as catalyst in many reaction due to :

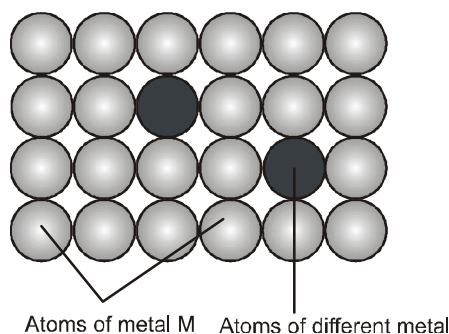
- (i) Possibility of variable oxidation state
- (ii) Presence of free valencies over metal surface (adsorption power)
- (iii) Presence of vacant d-orbital

e.g.



(N) ALLOY FORMATION :

Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and therefore the atoms of one metal can substitute the atoms of other metal in its crystal lattice.



Alloy formation

Note : Fe, Co, Ni do not form amalgam with Hg (Due to large difference in size)

BEGINNER'S BOX-1

1. The general electronic configuration of d-block elements is $(n-1)d^{1-10} ns^{1-2}$. This generalisation has several exceptions mainly due to
 - (1) strong shielding of $(n-1)$ d-electrons
 - (2) very little energy difference between $(n-1)d$ and ns orbitals
 - (3) presence of unpaired electrons
 - (4) high energy difference between $(n-1)d$ and ns orbitals
2. Select group of transition elements
 - (1) Pb, Sc, V
 - (2) Pd, Cd, La
 - (3) Pd, La, Fe
 - (4) Zn, Pd, Bi
3. Which element is having lowest melting and boiling point :
 - (1) Ti
 - (2) Cu
 - (3) Zn
 - (4) Mn



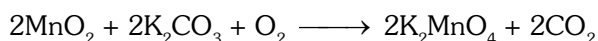
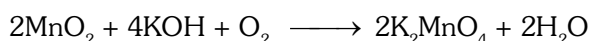
4. Density of which of the following element is highest
 (1) Pt (2) Hg (3) Mn (4) Cu
5. Not more than one oxidation state is shown by :
 (1) Mn (2) Cr (3) Fe (4) Sc
6. Consider the ions Fe^{2+} , Fe^{3+} , Cr^{2+} , Cr^{3+} , Mn^{2+} , Mn^{3+}
 (i) Strongest oxidising ion is
 (1) Fe^{2+} (2) Cr^{3+} (3) Mn^{3+} (4) Mn^{2+}
 (ii) Strongest reducing ion is
 (1) Fe^{2+} (2) Mn^{2+} (3) Cr^{2+} (4) Mn^{3+}
7. Which compound does exist
 (1) MnO_3F (2) $\text{K}_2[\text{CuI}_4]$ (3) MnF_7 (4) CrF_7
8. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because
 (1) Cr(VI) is more stable than Mo(VI) & W(VI)
 (2) Mo(VI) and W(VI) are less stable than Cr(VI)
 (3) H.O.S. of heavier members of group 6 of transition metals are more stable
 (4) L.O.S. of heavier members of group 6 of transition metals are more stable
9. By which of the following species, a transitional metal can brought in to its highest oxidation state
 (1) F_2 (2) Cl_2 (3) Br_2 (4) I_2

2.2 COMPOUNDS OF d-BLOCK ELEMENTS :

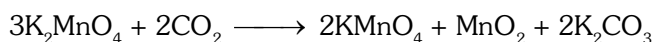
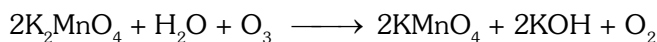
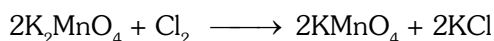
POTASSIUM PERMANGANATE (KMnO_4) :

(a) Preparation

This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidising agent such as KNO_3 . The fused mass turns green with the formation of potassium manganate, K_2MnO_4 .

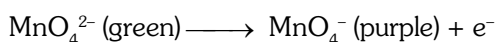


The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

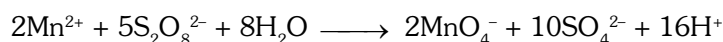


(disproportionate in acidic medium)

Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.



In the laboratory, a manganese(II) ion salt is oxidised by peroxodisulphate to permanganate

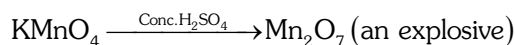


- (b) **Physical property :** It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

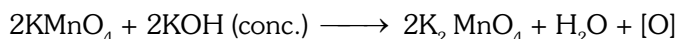


(c) Chemical property:

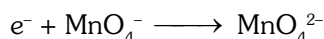
- **Effect of heating** $2\text{KMnO}_4 \xrightarrow{750\text{K}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
- On treatment with concentrated H_2SO_4 (KMnO_4 is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.



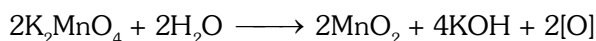
- Potassium permanganate is a powerful oxidising agent.
Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.
- In alkaline & neutral medium :
In strongly alkaline medium KMnO_4 is reduced to manganate.



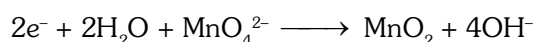
or



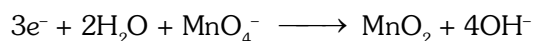
However if solution is dilute then K_2MnO_4 is converted into MnO_2 which appears as a brownish precipitate.



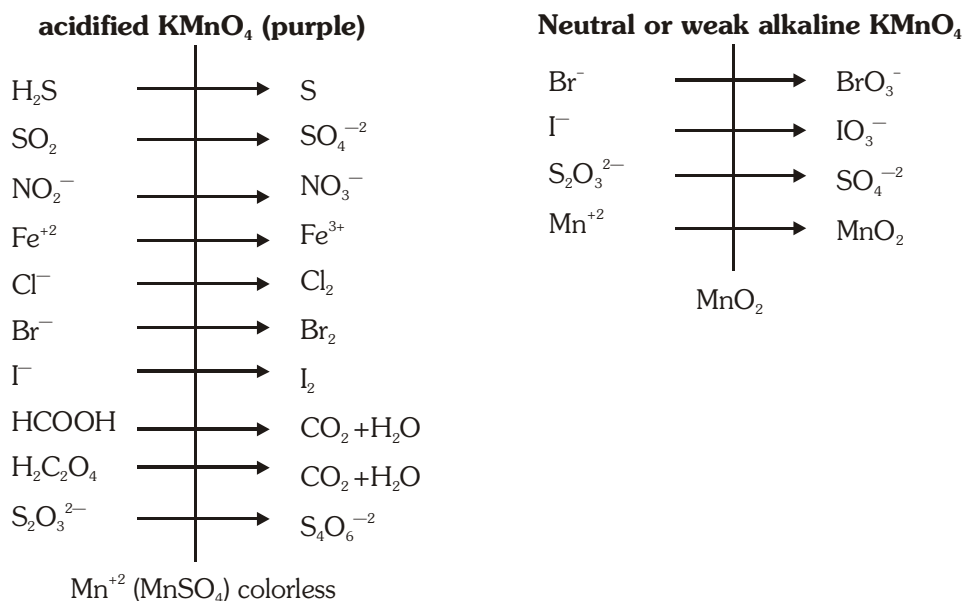
or



This type of behaviour is shown by KMnO_4 itself in neutral medium

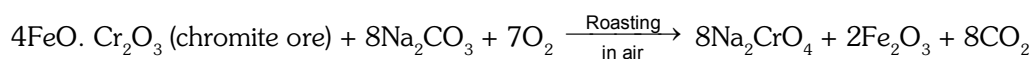


(d) Other reactions

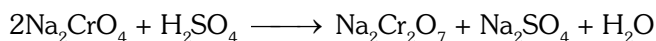


POTASSIUM DICHROMATE ($\text{K}_2\text{Cr}_2\text{O}_7$) :

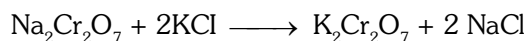
- (a) Preparation :** The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace



The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3 . The solution is then treated with calculated amount of H_2SO_4 .



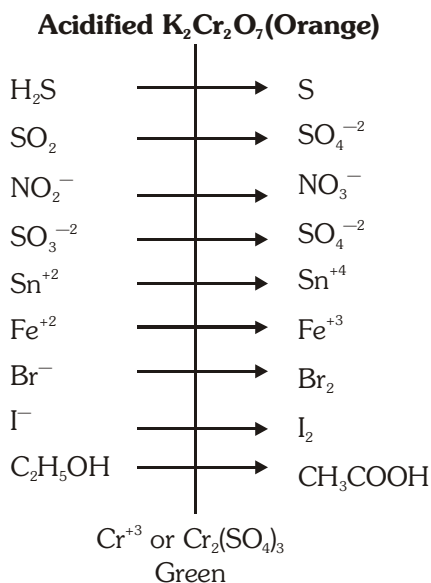
The solution is concentrated when less soluble Na_2SO_4 crystallises out. The solution is further concentrated when crystals of $\text{Na}_2\text{Cr}_2\text{O}_7$ are obtained. Hot saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ is then treated with KCl when orange red crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ are obtained on crystallisation.



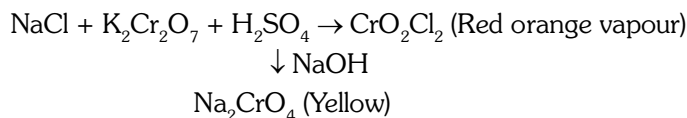
- $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{Na}_2\text{Cr}_2\text{O}_7$ as a primary standard in volumetric estimation because $\text{Na}_2\text{Cr}_2\text{O}_7$ is hygroscopic in nature but $\text{K}_2\text{Cr}_2\text{O}_7$ is not.
- $\text{CrO}_4^{2-} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Cr}_2\text{O}_7^{2-}$
- Solubility of $\text{Na}_2\text{Cr}_2\text{O}_7$ is higher than $\text{K}_2\text{Cr}_2\text{O}_7$
- (b) **Physical property :** It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C .
- (c) **Chemical property :**
 - **Effect of heating :** On strongly heating, it decomposes with liberating oxygen.



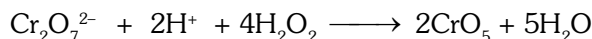
(d) **Other reactions**



1. **Chromyl chloride test :**



2. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution reacts with H_2O_2 in an ethereal solution to give a deep blue solution due to the formation of CrO_5 .



Note : Reaction with $\text{C}_2\text{H}_5\text{OH}$ is used in drunken driver test.



f-BLOCK ELEMENTS

2.3 INNER TRANSITION ELEMENTS

The elements in which the additional electron enters in $(n-2)f$ orbitals are called **inner transition elements** or **f-block elements**.

Position in The Periodic Table

The lanthanoids resemble with Yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanoid series (Z = 58 – 71) (Ce – Lu)

Actinide series (Z = 90 – 103) (Th – Lr)

2.4 LANTHANIDS (Rare Earths or Lanthanones)

- Lanthanoids are reactive elements so do not found in free state in nature.
- Most important minerals for lighter Lanthanoids are – Monazite, cerites and orthite and for heavier lanthanoids – Gadolinite and Xenotime

(a) Electronic configuration

- The general configuration of lanthanoids may be given as $[Xe] 4f^{1-14} 5s^2 5p^6 5d^{0-1} 6s^2$.

| Atomic No. | Element | Symbol | Outer electronic configuration | |
|------------|-------------------|-----------|---------------------------------------|-----------------------------|
| | | | Atomic | +3 ion |
| 58 | Cerium | Ce | $4f^1 5d^1 6s^2$ | $4f^1$ |
| 59 | Praseodymium | Pr | $4f^3 6s^2$ | $4f^2$ |
| 60. | Neodymium | Nd | $4f^4 6s^2$ | $4f^3$ |
| 61. | Promethium | Pm | $4f^5 6s^2$ | $4f^4$ |
| 62. | Samarium | Sm | $4f^6 6s^2$ | $4f^5$ |
| 63. | Europium | Eu | $4f^7 6s^2$ | $4f^6$ |
| 64. | Gadolinium | Gd | $4f^7 5d^1 6s^2$ | $4f^7$ |
| 65. | Terbium | Tb | $4f^9 6s^2$ | $4f^8$ |
| 66. | Dysprosium | Dy | $4f^{10} 6s^2$ | $4f^9$ |
| 67. | Holmium | Ho | $4f^{11} 6s^2$ | $4f^{10}$ |
| 68. | Erbium | Er | $4f^{12} 6s^2$ | $4f^{11}$ |
| 69. | Thulium | Tm | $4f^{13} 6s^2$ | $4f^{12}$ |
| 70. | Ytterbium | Yb | $4f^{14} 6s^2$ | $4f^{13}$ |
| 71. | Lutecium | Lu | $4f^{14} 5d^1 6s^2$ | $4f^{14}$ |

- It is to be noted that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium (Z = 64) with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.
- On the other hand, the filling of f-orbitals is regular in tripositive ions.
- After losing outer electrons, the f-orbitals shrink in size and became more stable.
- Pm** is the only synthetic radioactive lanthanoid.



(b) Oxidation states

- (i) In lanthanoids +3 oxidation state is most common.
- (ii) **Except Ce, Tb, Nd, Dy, Pr** which also exhibit +4.
- (iii) **Sm, Eu, Tm, and Yb**, also exhibit +2 state.

(c) Magnetic Properties

- (i) In tripositive lanthanoid ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0).
- (ii) lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanoid ions are paramagnetic. (Exception – Neodymium is the most paramagnetic lanthanoid).
- (iii) Ce^{+4} and Yb^{+2} are also diamagnetic ions.

(d) Colour

- (i) The lanthanoid ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f-f transition and hence exhibit colour.
- (ii) The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.
- (iii) The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.
- (iv) Lanthanoid ions having $4f^0$, $4f^{14}$ are colourless.

(e) Lanthanoid Contraction

- (i) In the lanthanoid series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanoid contraction.
- (ii) The general electronic configuration of these elements is $4f^{1-14}5s^26p^6d^{0-1}6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- (iii) Due to very poor shielding effect of (n-2)f electrons, they exert very little screening effect on the outermost $6s^2$ electrons.

Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

APPLICATIONS OF LANTHANOID CONTRACTION

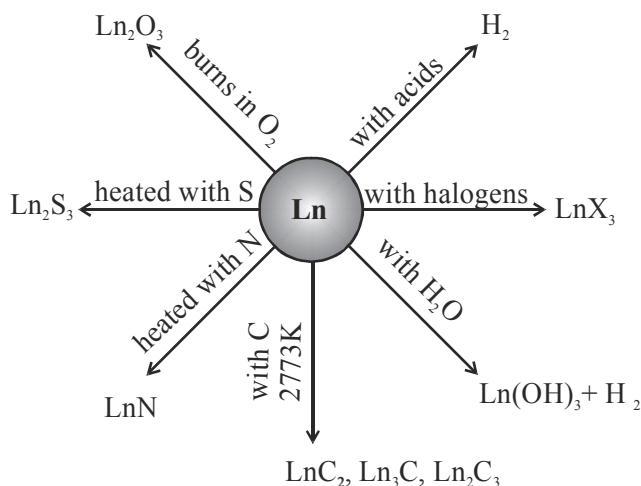
- **Atomic size :** The ionic radii of Zr^{+4} is about 9% more than Ti^{+4} . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4} , instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanoid contraction.

This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

- **Basic nature of hydroxide :** The effect of lanthanoid contraction basic nature of hydroxide regularly decreases.
- **Similarity in properties of lanthanoid :** Due to small difference in size the chemical properties of lanthanoids are similar and their separation is difficult.



(e) Important reactions of Lanthanoids



Mish metal is an alloy of lanthanoids (Mainly cerium) and iron.

2.5 ACTINOIDS OR (5f - SERIES)

- (i) The elements in which the extra electron enters 5f-orbitals of $(n - 2)$ th main shell are known as actinoids.
- (ii) The man-made eleven elements $\text{Np}_{93} - \text{Lr}_{103}$ are placed beyond uranium in the periodic table and are collectively called trans-uranium elements.
- (iii) Th, Pa and U first three actinoids are natural elements.

(a) Electronic Configuration

The general configuration of actinoids may be given as $[\text{Rn}] 5f^{1-14} 6d^{0,1,2} 7s^2$.

| Atomic No. | Elements | Symbol | Outer Electronic Configuration | |
|------------|-------------|--------|--------------------------------|-----------|
| | | | Atomic | +3 ion |
| 90 | Thorium | Th | $6d^2 7s^2$ | $5f^1$ |
| 91 | Proactenium | Pa | $5f^2 6d^1 7s^2$ | $5f^2$ |
| 92 | Uranium | U | $5f^3 6d^1 7s^2$ | $5f^3$ |
| 93 | Neptunium | Np | $5f^4 6d^1 7s^2$ | $5f^4$ |
| 94 | Plutonium | Pu | $5f^6 6d^0 7s^2$ | $5f^5$ |
| 95 | Americium | Am | $5f^6 6d^1 7s^2$ | $5f^6$ |
| 96 | Curium | Cm | $5f^7 6d^1 7s^2$ | $5f^7$ |
| 97 | Berkellium | Bk | $5f^9 6d^0 7s^2$ | $5f^8$ |
| 98 | Californium | Cf | $5f^{10} 6d^0 7s^2$ | $5f^9$ |
| 99 | Einsteinium | Es | $5f^{11} 6d^0 7s^2$ | $5f^{10}$ |
| 100 | Fermium | Fm | $5f^{12} 6d^0 7s^2$ | $5f^{11}$ |
| 101 | Mandeleium | Md | $5f^{13} 6d^0 7s^2$ | $5f^{12}$ |
| 102 | Nobellium | No | $5f^{14} 6d^0 7s^2$ | $5f^{13}$ |
| 103 | Lowrencium | Lr | $5f^{14} 6d^1 7s^2$ | $5f^{14}$ |

(b) Oxidation states

- (i) In lanthanoids and actinoids +3 oxidation is the most common for both of the series of elements.
- (ii) This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.



(iii) Highest oxidation states in the actinoids is +7 exhibited by Np_{93} & Pu_{94} , it is unstable.

(iv) Highest stable oxidation state is +6 shown by U_{92} .

Other Properties

- **Physical appearance** : Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalis.
- **Density** : All the actinoids except **thorium** and **americium** have high densities.
- **Colour** : Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled f-subshell) are colourless, as expected.
- **Ionisation energies** : Ionisation energies values of actinoids are low.
- **Electropositive character** : All the known actinide metals are **highly electropositive**. They resemble lanthanoid series in this respect.
- **Melting Boiling properties** : They have **high melting and boiling points**. They do not follow regular gradation of melting or boiling points with increase in atomic number.
- **Magnetic properties** : The actinide elements are paramagnetic due to the presence of unpaired electrons.
- **Radioactive nature** : All the actinoids are radioactive in nature.
- **Actinide contraction** : The size of atom/cation decrease regularly along the actinoids series. The steady decrease in ionic radii with increase in atomic number is referred to as **actinide contraction**. This is due to poor shielding of 5f-electrons.

Comparison of Lanthanides and Actinoids

Points of Resemblance :

- Both lanthanoids and actinoids show a dominant oxidation state of +3.
- Both are electropositive and act as strong reducing agents.
- Cations with unpaired electrons in both of them are paramagnetic.
- Most of the cations of lanthanoids and actinoids are coloured.
- Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanoids show **lanthanoid contraction** and actinoids show **actinide contraction**.

POINTS OF DISTINCTION

| Lanthanoids | Actinoids |
|---|---|
| 1. Besides the most common oxidation state of +3 lanthanoids show +2 and +4 oxidation states in case of certain elements. | Besides the most common oxidation state of +3, actinoids show +4, +5 and +6 oxidation states in case of certain elements. |
| 2. Lanthanoids have less tendency towards complex formation. | Actinoids have a stronger tendency towards complex formation. |
| 3. Except promethium, they are non radioactive. | All the actinoids are radioactive. |
| 4. Oxides and hydroxide of lanthanoids are less basic. | Oxides and hydroxides of actinoids are more basic |

Some important uses of actinoids are as follows –

Thorium : Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

Uranium : Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour). textile industry and also in medicines.

Plutonium : Plutonium is used as fuel for atomic reactors as well as in atomic bombs.



BEGINNER'S BOX-2

1. KMnO_4 can be acidified by
 (1) Dil. HCl (2) conc. H_2SO_4 (3) conc. HNO_3 (4) dil. H_2SO_4
2. $\text{NaCl} \xrightarrow[\text{X}]{\text{conc. H}_2\text{SO}_4}$ yellow green gas, X is
 (1) $\text{K}_2\text{Cr}_2\text{O}_7$ (2) MnO_2 (3) KMnO_4 (4) both (2) & (3)
3. $\text{X} \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7]{\text{conc. H}_2\text{SO}_4}$ red brown vapours. X can be
 (1) NaI (2) NaBr (3) Both (1) & (2) (4) None of these
4. $\text{X} \xrightarrow[\text{black coloured ore}]{\text{KOH, air}} \text{Y} \xrightarrow[\text{dark green}]{\text{H}^+} \text{Z} + \text{X}$
 an oxidising agent
 True statement is
 (1) X can't be MnO_2 (2) Y can be KMnO_4
 (3) Z can be K_2MnO_4 (4) step (1) is oxidation while step (ii) is disproportionation
5. $\text{X} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Y}; \text{Y} \xrightarrow{\text{SO}_2} \text{Z} + \text{SO}_4^{2-}$
 X and Y are oxy anion of Cr than oxidation state of Cr in X, Y, Z will be respectively
 (1) +3, +6, +6 (2) +6, +3, +6 (3) +6, +6, +6 (4) +6, +6, +3
6. When KMnO_4 solution is added to oxalic acid, solution, the decolourisation is slow in beginning but become instantaneous after some time because
 (1) CO_2 is a by product (2) Mn^{2+} acts as a catalyst
 (3) reaction is exothermic (4) MnO_4^- catalyzes the reaction
7. The elements from cerium (At.No. 58) to lutetium (At.No. 71) in which 4f energy levels are filled up are called :
 (1) lanthanides (2) rare earths (3) lanthanones (4) all the above
8. Which of the following is a lanthanide :
 (1) Ta (2) Rh (3) Th (4) Gd
9. The element with the electronic configuraton $[\text{Xe}]^{54} 4f^{14} 5d^1 6s^2$ is a
 (1) representative element (2) transition element
 (3) lanthanide (4) actinide
10. Name the three lanthanides which show +2 oxidation state also :
 (1) Sm, Tb, Gd (2) Sm, Eu, Yb (3) La, Gd, Lu (4) Yb, Pm, Sm

ANSWER KEY

| BEGINNER'S BOX-1 | Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
|------------------|------|---|---|---|---|---|-----|---|---|---|----|
| | Ans. | 2 | 3 | 3 | 1 | 4 | 3,3 | 1 | 3 | 1 | |
| | | | | | | | | | | | |
| BEGINNER'S BOX-2 | Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| | Ans. | 4 | 4 | 2 | 4 | 4 | 2 | 4 | 4 | 3 | 2 |



NCERT QUESTIONS (REASONING)

Q.1 Why do the transition elements have higher boiling & melting points ?

Ans. Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

Q.2 Give the main difference in oxidation states of transition elements & p-block elements.

Ans. (i) The variation of oxidation state in transition elements is in such a way that their oxidation state differ from each other by unity e.g. V^{+2} , V^{+3} , V^{+4} , V^{+5} . While in p block elements oxidation states normally differ by two due to inert pair effect.

(ii) Stability of higher oxidation state in transition elements increase down the group
e.g. Pt^{+4} is more stable than Pt^{+2}

While in p block elements lower oxidation state become increasingly stable down the group as result of inert pair effect.

Q.3 For the first series of transition metals the E^\ominus values are

| E^\ominus | V | Cr | Mn | Fe | Co | Ni | Cu |
|----------------|-------|-------|-------|-------|-------|-------|-------|
| (M^{2+}/M) | -1.18 | -0.91 | -1.18 | -0.44 | -0.28 | -0.25 | +0.34 |

Explain the irregularity in the above values.

Ans. This is because of irregular variation of ionization energies ($IE_1 + IE_2$) and also the sublimation energies which are much less for manganese and vanadium

Q.4 Zinc does not show variable valency because of :

(A) complete 'd' sub-shell (B) inert pair effect (C) $4s^2$ sub-shell (D) none.

Ans. $Zn = [Ar]^{18} 3d^{10} 4s^2$. Zinc has completely filled d-sub-shell so removal of electron from completely filled 4d sub-shell would be quite difficult. Thus it does not show variable valency.

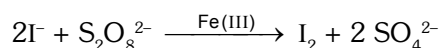
Q.5 Explain the blue colour of $CuSO_4 \cdot 5H_2O$.

Ans. Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Q.6 How iron (III) catalyses the reaction between iodide & persulphate?

Ans. $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$



EXERCISE-I (Conceptual Questions)

d-BLOCK ELEMENTS

- For a catalyst which condition is not essential :
(1) Variable valency
(2) High ionisation energy
(3) Empty orbitals
(4) Free valency on the surface
- To which of the following series the transition element from $Z = 39$ to $Z = 48$ belong :
(1) 3d series (2) 4d series
(3) 5d series (4) 6d series
- KMnO_4 on treatment with conc. H_2SO_4 forms a compound (X) which decomposes explosively on heating forming (Y). The (X) and (Y) are respectively
(1) Mn_2O_7 , MnO_2 (2) Mn_2O , Mn_2O_3
(3) MnSO_4 , Mn_2O_3 (4) Mn_2O_3 , MnO_2
- Which pair of ions is colourless :
(1) Mn^{3+} , Co^{3+} (2) Fe^{3+} , Cr^{3+}
(3) Zn^{2+} , Sc^{3+} (4) Ti^{2+} , Cu^{2+}
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is :
(1) Cr_2O_3 (2) CrO_2 (3) Cr_2O_4 (4) CrO_3
- $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[X]{X} 2\text{CrO}_4^{2-}$, X and Y are respectively
(1) $\text{X} = \text{OH}^-$, $\text{Y} = \text{H}^+$ (2) $\text{X} = \text{H}^+$, $\text{Y} = \text{OH}^-$
(3) $\text{X} = \text{OH}^-$, $\text{Y} = \text{H}_2\text{O}_2$ (4) $\text{X} = \text{H}_2\text{O}_2$, $\text{Y} = \text{OH}^-$
- During estimation of oxalic acid Vs KMnO_4 , self indicator is :
(1) KMnO_4 (2) Oxalic acid
(3) K_2SO_4 (4) MnSO_4
- The higher oxidation states of transition elements are found to be the combination with A and B, which are:
(1) F, O (2) O, N
(3) O, Cl (4) F, Cl
- Magnetic moment of x^{n+} is $\sqrt{24}$ B.M. Hence No. of unpaired electron and value of 'n' respectively. (Atomic number = 26)
(1) 4, 3 (2) 3, 5
(3) 4, 2 (4) 4, 1
- The product of oxidation of I $^-$ with MnO_4^- in alkaline medium is :
(1) IO_3^- (2) I_2 (3) IO^- (4) IO_4^-
- Copper becomes green when exposed to moist air for longer period.
(1) Because of the formation of a layer of cupric oxide on the surface of copper
(2) Because of the formation of a layer of basic carbonate of copper on the surface of copper
(3) Because of the formation of a layer of cupric hydroxide on the surface of copper.
(4) (1) and (3) both
- Which of the following oxide of chromium is amphoteric in nature
(1) CrO (2) Cr_2O_3
(3) CrO_3 (4) CrO_5
- Compared to Cu^{2+} having $3d^9$ configuration, Cu^+ having $3d^{10}$ configuration (aq. solution) :-
(1) Is more stable
(2) Is equally stable
(3) Is less stable
(4) Stability depends upon nature of copper salt
- Pick out the wrong statement :-
(1) $\text{K}_2\text{Cr}_2\text{O}_7$ reduces ferric sulphate to ferrous sulphate
(2) Iron do not form amalgam
(3) Permanent magnet is made by an alloy called Alnico
(4) In the Lathanides ionic radius decreases from La^{+3} to Lu^{+3}
- CrO_3 is red or orange in colour. The nature of oxide is :-
(1) Acidic (2) Basic
(3) Amphoteric (4) Neutral
- Cl_2 gas is obtained by various reactions but not by :
(1) $\text{KMnO}_4 + \text{conc. HCl} \xrightarrow{\Delta}$
(2) $\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$
(3) $\text{MnO}_2 + \text{conc. HCl} \xrightarrow{\Delta}$
(4) $\text{KCl} + \text{F}_2 \xrightarrow{\Delta}$



- 17.** Maximum magnetic moment is shown by :
 (1) d^5 (2) d^6
 (3) d^7 (4) d^8
- 18.** Disproportion can be shown by
 (1) MnO_4^{2-} in acidic medium
 (2) Cu^+ in aqueous medium
 (3) Cl_2 in alkaline medium
 (4) All of these
- 19.** The basic character of the transition metal monoxides follows the order :
 (Atomic no. Ti = 22, V = 23, Cr = 24, Fe = 26)
 (1) $TiO > FeO > VO > CrO$
 (2) $TiO > VO > CrO > FeO$
 (3) $VO > CrO > TiO > FeO$
 (4) $CrO > VO > FeO > TiO$
- 20.** Which of the following reactions is used to estimate copper volumetrically ?
 (1) $2Cu^{2+} + 4F^- \longrightarrow Cu_2F_2 + F_2$
 (2) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$
 (3) $2Cu^{2+} + 2CNS^- + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + H_2SO_4 + 2H^+$
 (4) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$
- 21.** Atomic size of gold is almost the same as that of silver. It is due to :
 (1) the same crystal structure of silver and gold
 (2) almost the same electropositive character of the two metals
 (3) transition metals contraction in a series
 (4) the effect of lanthanide contraction
- 22.** Which among the following statements is incorrect
 (1) In d-block elements oxidation state differ by unity.
 (2) In p-block metals oxidation state differ by two units.
 (3) In a group of p-block lower oxidation states are favoured by the heavier members.
 (4) In a group of d-block higher oxidation states are favoured by the lighter member.
- 23.** Which among the following order of oxidising character is correct—
 (1) $CrO_3 > MoO_3$ (2) $K_2Cr_2O_7 > KMnO_4$
 (3) $Fe(CO)_5 > Mn(CO)_5$ (4) $V_2O_3 > V_2O_5$
- 24.** Which of the following configurations of 3d series metals exhibits the largest number of oxidation states—
 (1) $[Ar] 3d^8 4s^2$ (2) $[Ar] 3d^{10} 4s^1$
 (3) $[Ar] 3d^5 4s^2$ (4) $[Ar] 3d^7 4s^2$
- 25.** Which of the following statement regarding interstitial compounds is incorrect—
 (1) They are chemically inert
 (2) They are soft and nonconductive
 (3) They retain metallic conductivity
 (4) They have high melting point.
- 26.** Which of the following pair of ions has same value of "spin-only" magnetic moment
 (1) Cu^+, Cu^{2+} (2) Co^{3+}, Fe^{2+}
 (3) Ti^{2+}, V^{2+} (4) Sc^{2+}, Zn^{+2}

f-BLOCK ELEMENTS

- 27.** The elements from thorium (At.No. 90) to lawrencium (At.No. 103) in which 5f energy levels are filled up are called :
 (1) lanthanides (2) rare earths
 (3) actinides (4) transuranics
- 28.** Select the element in the following which does not show +4 oxidation state :
 (1) Ti (2) Zr
 (3) La (4) Pt
- 29.** With increase in atomic number the ionic radii of actinides :
 (1) contract slightly
 (2) increase gradually
 (3) show no change
 (4) change irregularly
- 30.** The general electronic configuration of lanthanide is :
 (1) $[Xe] 4f^{14} 5d^{0-1} 6s^2$
 (2) $[Xe] 4f^{0-14} 5d^{1-2} 6s^1$
 (3) $[Xe] 4f^{0-14} 5d^{0-1} 6s^{1-2}$
 (4) None of these



- 31.** Cerium can show the oxidation state of +4 because
 (1) it resemble alkali metals
 (2) it has very low value of I.E.
 (3) of its tendency to attain noble gas configuration of xenon
 (4) of its tendency to attain $4f^7$ configuration
- 32.** In aqueous solution Eu^{+2} acts as :
 (1) an oxidising agent
 (2) reducing agent
 (3) can act as redox agent
 (4) None of these
- 33.** The maximum oxidation state shown by actinides is :
 (1) +6 (2) +7
 (3) +5 (4) +4
- 34.** The outer electronic configuration of gadolinium (At. No. 64) is :
 (1) $4f^7 5d^1 6s^2$ (2) $4f^8 5d^0 6s^2$
 (3) $4f^8 5d^1 6s^1$ (4) $4f^7 5d^0 6s^2$
- 35.** The most characteristic oxidation state of lanthanides is :
 (1) +2 (2) +3
 (3) +4 (4) none of these
- 36.** The common oxidation state of actinides is :
 (1) +4 (2) +3
 (3) +5 (4) +6
- 37.** Which of the following f - block elements, will change its group on emitting α -particle (alpha particle) :
 (1) ${}_{58}\text{Ce}$ (2) ${}_{70}\text{Lu}$
 (3) ${}_{90}\text{Th}$ (4) ${}_{92}\text{U}$
 Correct answer is :-
 (1) Only 1 and 3 (2) Only 2 and 4
 (3) All (4) None
- 38.** Which of the following pair have almost similar size
 (1) Ti_{22} and Zr_{40} (2) Nb_{41} and Ta_{73}
 (3) Y_{39} and La_{57} (4) Ca_{20} and Ir_{31}
- 39.** An increase in both atomic and ionic radii with atomic number occurs in any group of the periodic table. In accordance of this the ionic radii of Ti (IV) and Zr (IV) ions are 0.68 \AA and 0.74 \AA respectively but for Hf (IV) ion the ionic radius is 0.75 \AA , which is almost the same as that for Zr (IV) ion. This is due to :-
 (1) greater degree of covalency in compounds of Hf^{4+}
 (2) Lanthanide contraction
 (3) Difference in the co-ordination number of Zr^{+4} and Hf^{+4} in their compounds
 (4) Actinide contraction

| EXERCISE-I (Conceptual Questions) | | | | | | | | | | ANSWER KEY | | | | | |
|-----------------------------------|----|----|----|----|----|----|----|----|----|------------|----|----|----|----|----|
| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Ans. | 2 | 2 | 1 | 3 | 1 | 1 | 1 | 1 | 3 | 1 | 2 | 2 | 3 | 1 | 1 |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | 2 | 1 | 4 | 2 | 4 | 4 | 4 | 1 | 3 | 2 | 2 | 3 | 3 | 1 | 4 |
| Que. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | | | | | | |
| Ans. | 3 | 2 | 2 | 1 | 2 | 2 | 1 | 2 | 2 | | | | | | |



Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion** : 1st ionisation potential of mercury is greater than cadmium
Reason : Hg has stable electronic configuration ($5d^{10} 6s^2$)
 (1) A (2) B (3) C (4) D
- Assertion** : Zr and Hf have about the same atomic radius.
Reason : Zr and Hf lies in the same group.
 (1) A (2) B (3) C (4) D
- Assertion** : Zn, Cd, Hg are non-transition elements while Cu, Ag, Au are transition element
Reason : In Zn, Cd, Hg ($n - 1$)d orbitals are completely filled in their atomic state where as in Cu, Ag, Au they are incomplete.
 (1) A (2) B (3) C (4) D
- Assertion** : Cu^+ is more stable than Cu^{+2}
Reason : ΔIP is greater than 16 eV
 (1) A (2) B (3) C (4) D
- Assertion** : $KMnO_4$ is dark pink coloured compound
Reason : In the $KMnO_4$ charge transfer spectrum occurs.
 (1) A (2) B (3) C (4) D
- Assertion** : Hg is the only metal which is liquid at $0^\circ C$.
Reason : It has very high IP and weak metallic bond
 (1) A (2) B (3) C (4) D
- Assertion** : Valency of transition elements is variable
Reason : Energy of ns and $(n-1)d$ orbital is almost same.
 (1) A (2) B (3) C (4) D
- Assertion** : Melting point of Mn less than that of Fe
Reason : Mn has less number of unpaired e^- than Fe in atomic state
 (1) A (2) B (3) C (4) D
- Assertion** : Solution of Na_2CrO_4 in water is intensely coloured.
Reason : Ox. state of Cr in Na_2CrO_4 is +6.
 (1) A (2) B (3) C (4) D
- Assertion** : Ce^{+4} acts as oxidising agent in aqueous medium
Reason : +4 is common oxidation state of lanthanides
 (1) A (2) B (3) C (4) D
- Assertion** : Neptunium is transuranic element.
Reason : It is heavier than uranium
 (1) A (2) B (3) C (4) D
- Assertion** : $La(OH)_3$ is more basic than $Lu(OH)_3$
Reason : Lanthanum is d-block element
 (1) A (2) B (3) C (4) D
- Assertion** : Actinides show much higher range of oxidation states
Reason : Energy difference between 5f and 6d orbitals is large
 (1) A (2) B (3) C (4) D
- Assertion** : All the lanthanide elements exhibits a common oxidation state of +3 in their compounds.
Reason : The atoms of the lanthanide elements contains three electron in their outermost shell.
 (1) A (2) B (3) C (4) D



15. **Assertion:-** $K_2Cr_2O_7$ is used as a primary standard in volumetric analysis.
Reason:- It has a good solubility in water.
 (1) A (2) B (3) C (4) D
16. **Assertion:-** Change in colour of acidic solution of potassium dichromate by breath is used to test drunk drivers.
Reason:- Change in colour is due to the complexation of alcohol with potassium dichromate.
 (1) A (2) B (3) C (4) D
17. **Assertion:-** Eu^{2+} & Yb^{2+} are reducing agents for their ions.
Reason:- Both ions have stable half filled configuration.
 (1) A (2) B (3) C (4) D
18. **Assertion :-** MnO_2 is anti ferromagnetic in nature.
Reason :- In MnO_2 , equal number of domain are aligned with parallel and antiparallel spin.
 (1) A (2) B (3) C (4) D
19. **Assertion :-** La_2O_3 is basic nature.
Reason :- La in aqueous solution gives $La(OH)_3$
 (1) A (2) B (3) C (4) D
20. **Assertion :-** $FeCl_3$ does not affect iodometric titration of $CuSO_4$ Solution
Reason :- FeI_3 is formed.
 (1) A (2) B (3) C (4) D
21. **Assertion :-** Actinoids can posses +4 O.S. more easily then lanthanoid.
Reason :- 4f, 5d, 6s have almost same energy levels.
 (1) A (2) B (3) C (4) D
22. **Assertion :-** UF_6 is more covalent than UF_4 .
Reason :- Fluorine is smaller in size.
 (1) A (2) B (3) C (4) D

EXERCISE-II(Assertion & Reason)

ANSWER KEY

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|------|----|----|----|----|----|----|----|---|---|----|----|----|----|----|----|
| Ans. | 2 | 2 | 3 | 4 | 1 | 1 | 1 | 3 | 2 | 3 | 1 | 2 | 3 | 3 | 3 |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | | | | | | | | |
| Ans. | 3 | 3 | 1 | 1 | 4 | 2 | 2 | | | | | | | | |

